**TRANSLATION FROM JAPANESE**

(19) JAPANESE PATENT OFFICE (JP)
(11) Unexamined Patent Application (Kokai) No. **60-115699**
(12) Unexamined Patent Gazette (A)
(51) Int. Cl.[4]: Identification Symbol : JPO File No.:
C11B 9/02 6556-4H

(43) Disclosure Date: June 22, 1985
Request for Examination: Not filed
Number of Inventions: 1
(6 pages total [in original])

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(54) Title of the Invention: **Recovery process for hop essential oil**

(21) Application No. 58-223590
(22) Filing Date: November 28, 1983
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# SPECIFICATION

## 1. Title of the Invention

Recovery process for hop essential oil

## 2. Claims

1. A recovery process for hop essential oil in which hop essential oil contained in vapor discharge from the wort boiling process in beer production is isolated from said vapor discharge, wherein said process is characterized in that hop essential oil is recovered selectively by subjecting said vapor discharge to a process comprising the following steps:

A a step wherein the vapor discharge is cooled to a temperature within the range of 30 to 70°C;

B a washing step wherein the cooled vapor discharge is brought into contact with an aqueous solution at from 5 to 40°C;

C a step wherein the washed vapor discharge is brought into contact with a solid adsorbent, whereby hop essential oil contained in the vapor discharge is adsorbed onto said adsorbent; and

D a step wherein the adsorbent having adsorbed the hop essential oil is treated with a solvent for the hop essential oil in order to elute the hop essential oil.

2. The method according to claim 1, wherein the aqueous solution employed in step B is a sodium hypochlorite aqueous solution, copper sulfate aqueous solution, or 2,4-dinitrophenylhydrazine acidic aqueous solution.

## 3. Detailed Description of the Invention

### Background of the Invention

The present invention relates to a recovery process for hop essential oil, and more particularly to a method for selectively isolating and recovering hop essential oil from the vapor discharge of a wort boiler during the beer production process.

Hop essential oil is a yellow oily substance containing as principal components terpene hydrocarbons (e.g., humulene, selinene, cadinine, myrcene, etc.) that distill out during steam distillation of hops. Not only is it useful as a flavoring, but the physiological activity of the terpene hydrocarbons give it potential as a pharmaceutical ingredient.

In beer production, hops are added to the mash (which consists mainly of malt) and boiled, a process termed wort boiling. The principal object of the wort boiling process is to elute insoluble bitter substances from the hops into the wort, while at the same time inducing flocculation of heat-coagulating proteins in the wort. During this process, hop essential oil is emitted from the wort boiler together with steam and volatiles present in the wort. The wort boiler vapors have a characteristic odor produced by the substances contained therein, including hop essential oil, and measures for reducing odors by processing thereof have been researched in the past. There has been proposed a method for eliminating the odor components all at once by chilling of the wort boiler vapors and treatment with activated carbon (Hamano, "Sangyo to Kankyo", 84 (1982)).

In the wort boiling process, most of the hop essential oil in the hops is exhausted in the form of wort boiler vapor discharge together with steam and other volatiles. The literature reveals no reported attempts to selectively recover this hop essential oil from the wort boiler vapor discharge.

## Summary of the Invention

### Gist

The present invention has as an object to selectively recover hop essential oil exclusively while removing other odor components present in wort boiler vapor discharge, this object being achieved by carrying out a process comprising specific individual steps purposefully combined together.

Specifically, the hop essential oil recovery process of the invention provides a method by which hop essential oil contained in vapor discharge from the wort boiling process in beer production is isolated from said vapor discharge, characterized in that hop essential oil is recovered selectively by subjecting said vapor discharge to a process comprising the following steps:

A a step wherein the vapor discharge is cooled to a temperature within the range of 30 to 70°C;

B a washing step wherein the cooled vapor discharge is brought into contact with an aqueous solution at from 5 to 40°C;

C a step wherein the washed vapor discharge is brought into contact with a solid adsorbent, whereby hop essential oil contained in the vapor discharge is adsorbed onto said adsorbent; and

D a step wherein the adsorbent having adsorbed the hop essential oil is treated with a solvent for the hop essential oil in order to elute the hop essential oil.

Effects of the Invention

According to the present invention, by means of a simple process which is a combination of a conventional operation (basically consisting of a chilling step and an adsorption step) with a wet-process washing step with a liquid, and a step for eluting and recovering the hop essential oil, odor components present in wort boiler vapor discharge may be substantially completely removed while allowing the useful component, namely, hop essential oil, to be recovered selectively. Hop essential oil recovered using the method of the invention has qualities (i.e., organoleptic fragrance/flavor and a gas chromatography profile) identical to those of hop essential oil produced by steam distillation of hops. The cooling water used in step A (cooling step) can be utilized effectively for recovery and utilization of waste heat.

## Detailed Description of the Invention

The method of the invention basically consists of four steps: (1) cooling the wort boiler vapor discharge; (2) wet-process washing with a liquid; (3) adsorption; and (4) elution/recovery.

In beer production, the wort, together with hops, is boiled for about one to two hours in the wort boiler. The vapors emitted from the wort boiler at this time (at about 90-100°C) contain steam; hop essential oil consisting principally of terpenes (e.g., humulene, selinene, cadinine, myrcene, etc.); and wort-derived fatty acids, phenols, alcohol, aldehydes, esters, furans, hydrocarbons, ketones, lactones, pyrazines, pyrroles, sulfides, glycerides, and other odor substances. As used herein, hop essential oil refers to the yellow oily substance containing the aforementioned terpenes, that distills out with steam distillation of hops; this is typically contained in hops in amounts of from 0.1 to 2.0%.

Wort boiler vapor discharge cooling step

The vapors (about 90-100°C) emitted from the wort boiler are directed into a condenser and cooled to a vapor temperature of about 30 to 70°C. In this step, most of the steam present in the vapor discharge is collected as condensation, with the high-boilers (glycerides, fatty acids, etc.), hydrophilic components (phenols, etc.), and unpleasant odor components (pyrazines, pyrroles, etc.) being removed via condensation or dissolving into the condensed water.

Wet-process washing step with a liquid

The vapor, having been cooled to about 30 to 70°C, is now directed to a gas washing apparatus of a type known in the art, where it is subjected to thorough wet-process washing by bringing it into contact with an aqueous solution of a suitable chemical agent (at 5 to 40°C, and usually at ambient temperature). With this process, the temperature of the vapor drops to about 40°C. Suitable chemical agents include acids and alkalis known in the art (e.g., HCl, $H_2SO_4$, NaOH, etc.), oxidizing agents (e.g., hydrogen peroxide, hypochlorites, potassium permanganate, etc.), surfactants (e.g., propylene glycol, etc.), metal salts (e.g., copper sulfate, acetates, etc.), carbonyl reaction reagents (e.g., 2,4-dinitrophenylhydrazine), and the like in aqueous solution of about 0.01 to 5% [concentration]. Sodium hypochlorite aqueous solution, copper sulfate aqueous solution, and 2,4-dinitrophenylhydrazine acidic aqueous solution are especially effective. In this step, odor components (other than the hop essential oil) present in the wort boiler vapor discharge are substantially completely removed. The wet-process washing apparatus can be of any configuration suited to the purpose at hand, provided that the vapors being treated can be brought into contact with the aqueous washing solution. Examples are a spray column or packed column. Prior to wet-process washing with the chemical liquid, it is effective, in terms of preventing degradation of the chemical liquid in the chemical liquid wet-process washing process, to first subject the vapor from the cooling step (about 30 to 70°C) to a washing process with water (at ambient temperature). The "contact with an aqueous solution" of step B of the invention includes treatment with water per se (used either as a preliminary treatment, or for treatment proper).

Adsorption step

The vapor (about 40°C or lower) from the chemical liquid wet-process washing process is directed to an adsorption apparatus packed with a suitable adsorbent in order to adsorb the hop essential oil. Suitable adsorbents must fulfill the following two conditions: (1) being able to efficiently adsorb the hop essential oil; and (2) being capable of eluting the adsorbed hop essential oil with the use of a solvent in the elution/recovery step. As specific examples, activated carbon and the styrene-divinylbenzene synthetic porous adsorbents AMBERLITE XAD (ex Rohm & Haas) and DIAION HP (ex Mitsubishi Chemical Industry) are particularly effective.

P. Wright p 6-7

Elution/recovery step

The adsorbent having adsorbed the hop essential oil is brought into contact with a solvent for the hop essential oil in order to elute the hop essential oil; the hop essential oil can be recovered from the resultant solution by concentration under

partial vacuum. Suitable solvents will be capable of effectively eluting the hop essential oil from the adsorbent; as specific examples dichloromethane and liquid hydrocarbons are especially good for activated carbon adsorbents, and dichloromethane, liquid hydrocarbons, hexane, ethanol and the like for AMBERLITE XAD or DIAION HP.

## Examples

### Example 1

Wort boiler vapor (120 $m^3$/min) at about 100°C was directed into a condenser (heat transfer area 74.5 $m^2$) through which was circulated cold water (about 20°C) to bring the vapor temperature down to about 60°C. A portion of the gas flow (16.6 $m^3$/min) was passed at a flow rate of about 0.8 m/sec through water (about 20°C; water circulated at 220 liters/min) and then through a wet-process washing apparatus (spray column) through which was circulated 0.1% sodium hypochlorite aqueous solution (about 20°C; liquid circulated at 130 liters/min). A portion of the gas flow (21.7 $m^3$/hr) having reached 30-35°C was passed at a flow rate of about 0.3 m/sec through an activated carbon column packed with 6 kg of activated carbon. 10 g of activated carbon, through which had passed a total of 5121 $m^3$ of vapor, were washed thoroughly in 200 mL of dichloromethane and filtered. The dichloromethane was distilled off, yielding hop essential oil at a rate of 98 g/kg activated carbon.

### Example 2

Following the procedure of Example 1, but using a 500 ppm [aqueous solution of] the surfactant TWEEN 80 (ex Atlas Powder) instead of 0.1% sodium hypochlorite aqueous solution, hop essential oil was prepared at a rate of 85 g/kg activated carbon.

### Example 3

Following the procedure of Example 1, but using a 1000 ppm [aqueous solution of] the oxidizing agent hydrogen peroxide instead of 0.1% sodium hypochlorite aqueous solution, hop essential oil was prepared at a rate of 72 g/kg activated carbon.

### Example 4

Following the procedure of Example 1, but using a 1% metal salt (copper sulfite) solution instead of 0.1% sodium hypochlorite aqueous solution, hop essential oil was prepared at a rate of 108 g/kg activated carbon.

### Example 5

Following the procedure of Example 1, but using a dilute sulfuric acid solution of a functional group reaction reagent (2,4-dinitrophenylhydrazine) solution instead of 0.1% sodium hypochlorite aqueous solution, hop essential oil was prepared at a rate of 105 g/kg activated carbon.

Example 6

Following the procedure of Example 1, but using the synthetic porous adsorbent AMBERLITE XAD instead of activated carbon, hop essential oil was prepared at a rate of 103 g/kg AMBERLITE XAD.

Example 7

Following the procedure of Example 6, but using the nonpolar solvent hexane instead of dichloromethane, hop essential oil was prepared at a rate of 49 g/kg AMBERLITE XAD.

Example 8

Following the procedure of Example 1, but using liquefied $CO_2$ instead of dichloromethane, hop essential oil was prepared at a rate of 95 g/kg activated carbon.

Comparative Example 1

Wort boiler vapor (120 $m^3$/min) at about 100°C was directed into a condenser (heat transfer area 74.5 $m^2$) through which was circulated cold water (about 20°C) to bring the vapor temperature down to about 60°C. The vapor was then directed into another condenser (heat transfer area 74.5 $m^2$) through which was circulated cold water (about 20°C) to bring the vapor temperature down to about 35°C. A portion of the gas flow (21.7 $m^3$/min) was passed at a flow rate of about 0.3 m/sec through an activated carbon column packed with 6 kg of activated carbon. 10 g of activated carbon, through which had passed a total of 2000 $m^3$ of vapor, were washed thoroughly in 200 mL dichloromethane and filtered. The dichloromethane was distilled off, yielding hop essential oil at a rate of 163 g/kg activated carbon.

Experimental Example

[The products prepared in] the preceding Examples and Comparative Example were evaluated in terms of wort boiler vapor odor concentration after a deodorization process and the quality of the resultant hop essential oils; results are summarized in Table 1.

(1) Measurement of odor concentration

Three-point comparison odor bag method ([described in "Showa 52 Nendo Kanno Shiken Chosa Hokoku Sho" [1997 Organoleptic Test Survey Report], the Special Pollution Division of the Air Quality Bureau of the Environment Agency, March 1978).

(2) Hop essential oil quality evaluation

Organoleptic tests and gas chromatography analysis (3 mm x 2 m column, CARBOWAX 20 M packing) were performed, comparing the results with those for commercially available hop essential oil (ex US Calsec).

Table 1

| | | Wort boiler vapor odor concentration | | Recovered hop oil quality* | |
|---|---|---|---|---|---|
| | | Before processing | After processing | Organoleptic | Gas chromatogram |
| Examples | 1 | 97,000 | < 30 | O | O (Fig. 2) |
| | 2 | " | < 50 | O | O |
| | 3 | " | " | O | O |
| | 4 | " | " | O | O |
| | 5 | " | " | O | O |
| | 6 | " | < 100 | O | O |
| | 7 | " | < 100 | O | O |
| | 8 | " | < 30 | O | O |
| Comp. Ex. 1 | | " | < 100 | X | X (Fig. 3) |

*In the recovered hop essential oil quality evaluation, an "O" indicates quality similar to commercially available hop essential oil, while an "X" indicates a significant difference.

## 4. Brief Description of the Drawings

Fig. 1 is a gas chromatogram for commercially available hop essential oil;

Fig. 2 is a gas chromatogram for the hop essential oil recovered in Example 1; and

Fig. 3 is a gas chromatogram for the odor substances, including hop essential oil, recovered in Comparative Example 1.

S: solvent peak

hatched portions: peak for component not present in Fig. 1

Fig. 1

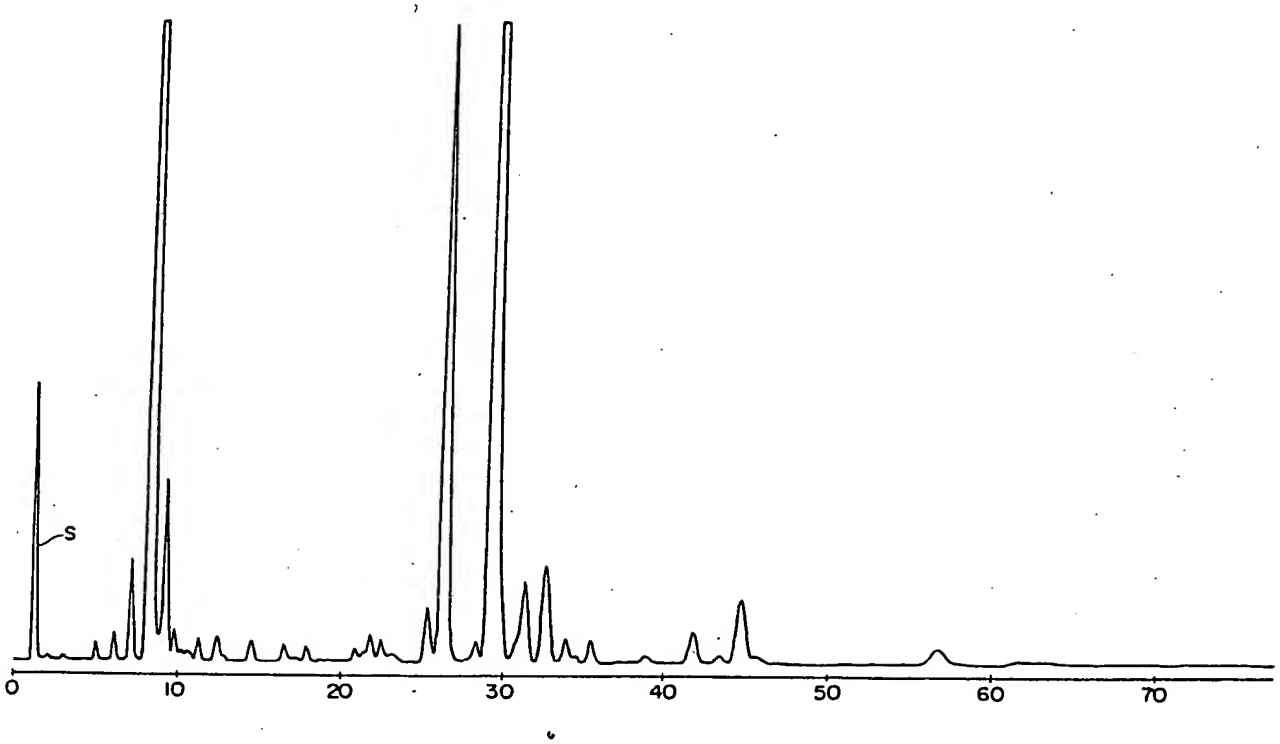
S
0
10
20
30
40
50
60
70
RETENTION TIME (MIN)

Fig. 2

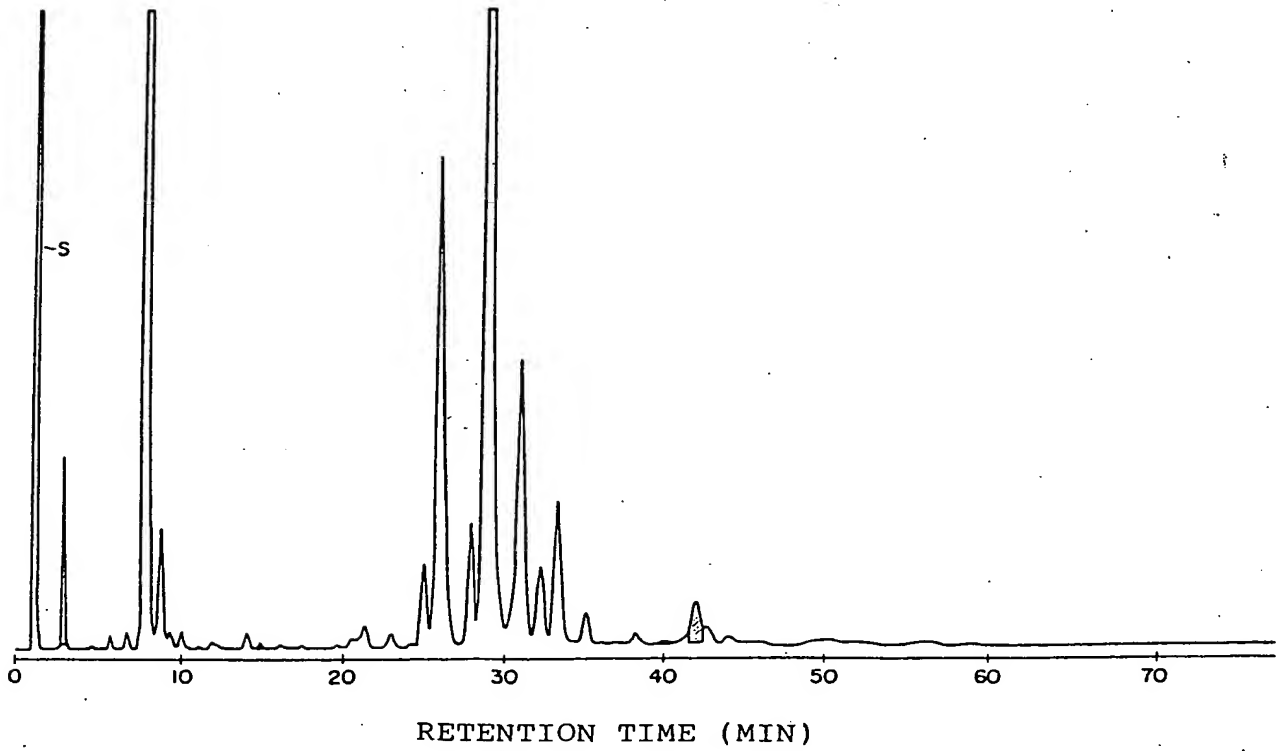
S
0
10
20
30
40
50
60
70
RETENTION TIME (MIN)

Fig. 3